

A steady increase of molybdenum in the precipitate was observed with increasing content of this metal in the alloys up to 50%. A sharp reduction of its content in the precipitate occurred after the further increase of its content in the alloy. Evidently, various boride phases were formed in these alloys: an insoluble one (under the given experimental conditions) and a soluble one. The amount of the undissolved phase rises with increased molybdenum content in the alloy up to 50%. The soluble boride phase passed into solution along with the metallic bond (excess molybdenum).

These results were checked by another method based on chemical dissolution of metallic molybdenum and of the soluble boride phase in hydrogen peroxide, while the insoluble boride phase remained without decomposition in this solvent.

An alloy sample of 0.1 g was placed into a 300 ml beaker and 75 ml of 30% hydrogen peroxide was added. The beaker was covered with a watch glass and heated for two hours at 50° on a water bath, with periodic stirring. The precipitate was allowed to settle and this then filtered off through a dense paper filter and washed with water until the test for hydrogen peroxide with a titanium salt solution became negative. 20 ml of sulfuric acid (1:2) was added to the filtrate, the solution was concentrated until vapors of sulfur trioxide appeared, the residue was diluted with water and transferred into a volumetric flask. The molybdenum content was determined in the precipitate and in the filtrate. The experimental results, shown in Table 3, confirmed the data obtained from the use of the electrochemical alkaline method, but the former were more distinct and reproducible.

Chemical methods of separation as for example a treatment with hydrogen peroxide, which may be suitable for the separation of chromium diboride and double diboride of chromium and titanium from titanium diboride — may also be used in cases of the presence of several carbides or borides in the principal phase. In the example above, the chromium diboride and the double diboride remain without decomposition, while titanium diboride dissolves.

DETERMINATION OF LOW CONCENTRATIONS BY THE METHOD OF DIFFERENTIAL OSCILLOGRAPHIC POLAROGRAPHY

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The substance of the method of differential oscillographic polarography, developed by N. M. Pozdeev [1, 2], consists of a simultaneous electrolysis of two identical solutions, one of which contains the substance being determined. The screen of the oscillograph shows a curve, which corresponds to the difference of current densities of the two electrolytic cells and which is close in shape to the theoretical curve, provided that the appropriate conditions had been fulfilled [1]. The differential method permits one to materially reduce the effect of the capacity current, of oxygen and of the more electropositive elements on the sensitivity and the accuracy of the determination.

We developed a method for quantitative determination of low concentrations of cadmium, lead, bismuth and zinc in presence of all of them in the solution, this method being that of a differential oscillographic polarography. For the work we used the apparatus assembled according to the main scheme suggested by N. M. Pozdeev. The block diagram and the electric circuit of the apparatus are shown in Fig. 1 and 2, respectively.

Two mercury dropping electrodes with dissimilar characteristics are used as the polarizing electrodes. The synchronization of drop formation and, thus, the reproducibility of the oscillograms, was attained by a forced removal of the mercury drops. The saw-tooth impulses were fed into the mercury dropping electrodes at strictly equal and regulated time intervals. A test of the setup was made with a mixture of equimolar solutions of

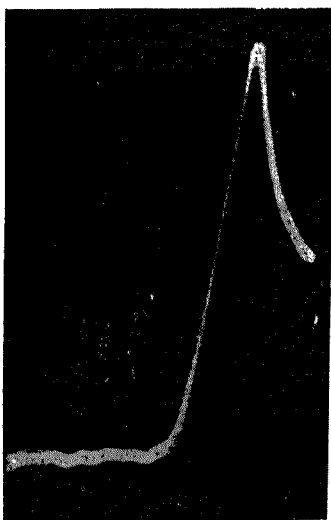


Fig. 3. Differential oscillographic polarogram of 10^{-4} gram-ions/liter of cadmium in the absence of dissolved oxygen; background: solution molar in respect to NH_4OH and NH_4Cl .

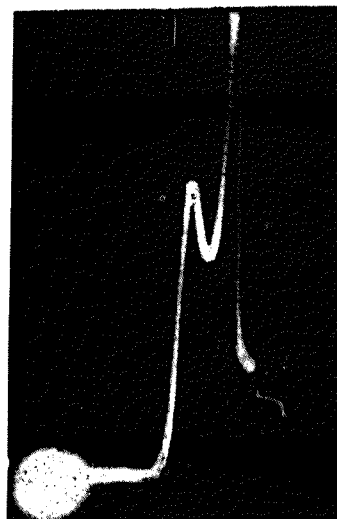


Fig. 4. Differential oscillographic polarogram of $1.5 \cdot 10^{-4}$ gram-ion/liter solution of cadmium in the presence of dissolved oxygen; background: M KCl solution.

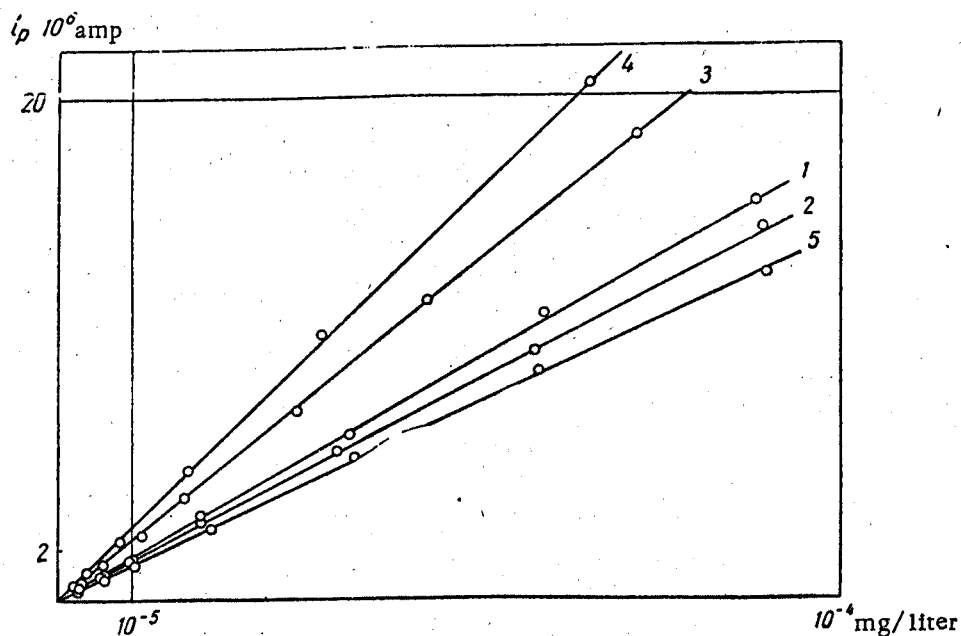


Fig. 5. Dependence of the current strength at wave peak (i_p) on the concentration of the ions in the presence of oxygen: 1) for cadmium ions with background of M HCl; 2) for cadmium ions with background of M NH_4OH and NH_4Cl ; 3) for lead ions with background of M HCl; 4) for bismuth ions with background of 0.4M CH_3COOH + 0.4M CH_3COONa + 0.01M Trilon; 5) for zinc ions with background of M NH_4OH + M NH_4Cl

An electrolysis of solutions of salts of cadmium, lead, zinc and bismuth in the presence and in the absence of dissolved oxygen was run for the determination of the effects of dissolved oxygen. An appearance of a second

TABLE 2

Results of Determination of Lead, Bismuth, Zinc and Cadmium

Cation	Taken, γ/ml	Addition, γ/ml	Found, after deduction of addition (average) γ/ml	Error, %
Pb	0.207	0.103; 0.207; 0.415; 0.620	0.217	+5.0
Bi	0.230	0.11; 0.23; 0.46; 0.69; 0.92	0.220	-5.0
Zn	0.130	0.066; 0.13; 0.26; 0.39; 0.52	0.120	-7.5
Cd	0.210	0.21; 0.42; 0.63; 1.05	0.200	-5.0

peak on the curve was noted in a number of cases; the wave height and the form of the oscillogram depended on the initial potential of electrolysis which fact greatly complicated the quantitative determinations. The distortion of the oscillograms (Fig. 4) which was observed for the cadmium ions in M KCl solution and for lead in 0.25 M $\text{KNaC}_4\text{H}_4\text{O}_6$ solution and in M KCl solution, could be explained, in accordance with the literature data [3, 4], by interaction of the metal ion with the hydroxyl ions which are the products of electroreduction of oxygen and by the formation of electrically active particles of $[\text{Me}(\text{OH})_2]_n$ in the near-electrode layer. If the formation of these particles is hindered by the high level of acidity of the solution or by buffer action and complex formation, the distortion of the oscillograms does not occur.

The dependence of the current strength at the wave peak on the concentration of the ion was studied for each ion in the presence of dissolved oxygen. It was established that, in agreement with the theory given in [5, 6], the current strength at the wave peak depends linearly on the concentration (Fig. 5) with a deviation in the interval of $5 \cdot 10^{-6}$ – $1 \cdot 10^{-6}$ M concentrations, the deviation being about 5-8%. The sensitivity of the cadmium determination, lead determination and bismuth determination was $1 \cdot 10^{-6}$ gram-ions/liter; that for zinc $2 \cdot 10^{-6}$ gram-ions/liter. It is possible to use a calibration curve, the methods of addition, etc., for the determinations.

Considering that it is rather difficult, in actual practice, to make up a solution for the second cell that would be identical in composition and concentration of the components in comparison with the first cell, it was necessary to determine how much does the difference in the composition and concentration of the solutions affect the accuracy of the determination. We studied the effect of the differences in concentrations of ammonia, ammonium chloride and hydrochloric acid on the shape and the wave height of cadmium ions. At M concentration of NH_4OH or NH_4Cl in the solution in the second cell with the cadmium ion concentration of $5 \cdot 10^{-6}$ M the variation of concentrations of these substances in the solution in the first cell was permissible within the limits of 0.8-1.2 M for NH_4Cl or 0.7-1.3 M for NH_4OH . At the content of 1 m/liter of hydrochloric acid and $2 \cdot 10^{-5}$ gram-ions/liter of cadmium, the permissible variation of the concentration of hydrochloric acid in the solution in the first cell was 0.7-1.3 m/liter (Table 1). The errors in the determination in these cases did not exceed the usual ones and the shape of the oscillograms was not deformed. With greater concentration differences, the conditions for the calculation of currents are considerable deteriorated and the errors increase.

The effect of an addition of sodium nitrate into the solution in the first cell was also studied in case of cadmium ions. If the nitrate is present in both cells, the permissible difference of its concentrations is 0.04 M at the concentration of 0.5 M.

The determination of cadmium, lead, bismuth and zinc ions, with their mutual presence, was performed by the method of additions. Cadmium and lead were determined with the background of M hydrochloric acid; bismuth with the background of 0.4 M CH_3COOH + 0.4 M CH_3COONa + 0.1 M Trilon; zinc with the background of M NH_4OH + M NH_4Cl + 0.1 M $\text{KNaC}_4\text{H}_4\text{O}_6$. Various amounts of the elements being determined were introduced into the control solution, to raise the accuracy of the determination, and the average result was determined graphically. The results of the determination of cadmium, lead, bismuth and zinc ions are given in Table 2.

In this manner it is possible by means of the differential oscillographic polarograph to make determinations of low concentrations of ions of cadmium, lead, bismuth and zinc. The sensitivity of the method is $1 \cdot 10^{-6}$ M;

the error within the concentration range of $5 \cdot 10^{-6} - 1 \cdot 10^{-6}$ M does not exceed 5-8%. A certain difference in the composition of the solutions does not hinder the determination.

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POLAROGRAPHIC DETERMINATION OF ALUMINUM

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The polarographic determination of aluminum is one of the difficult problems in polarography of metal ions. Aluminum salts are easily hydrolyzed in solutions with $\text{pH} > 4$ and the resulting diffusion current does not express the actual concentration of aluminum. In solutions with $\text{pH} < 3.2$ near the reduction potential of aluminum (-1.7 v on the background of magnesium chloride) there appears a hydrogen wave which hinders the determination of the true wave height of aluminum.

The polarographic methods of aluminum determination which have been described in the literature are mainly indirect ones.

For the development of a method of aluminum determination we used buffer solutions with $\text{pH} = 3.5-4$, having a large buffer capacity and, also, we used the ability of aluminum to form complex compounds with a number of organic acids [1].

The use of the buffer solution of Walpole type with $\text{pH} = 4.1$, containing 75 ml of 0.2N acetic acid and 80 ml of 0.2N sodium acetate failed to give satisfactory results. The complexes formed by aluminum with tartaric, citric and lactic acids have a high stability constant, the separation potential of a aluminum moves strongly in the negative direction and the aluminum wave cannot be seen, owing to the beginning of reduction of the background electrolyte. Weak complex-formers (glucose, glycerol, salicylic acid) generally do not retain aluminum in solution [2].

Similar results were obtained by us with the backgrounds of sodium oxalate and lithium citrate.

It was most satisfactory to use gluconic acid [3-5] in the form of its calcium salt. The appearance of a weak yellow-green color after the addition of a solution of calcium gluconate to the colorless solution of aluminum sulfate or aluminum potassium alum serves as a proof of the formation of a complex

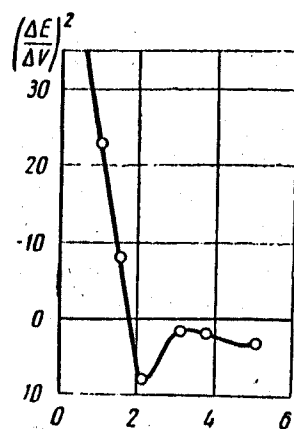


Fig. 1. Change of $\Delta^2 \text{pH} / \Delta v^2$ (expressed as $\Delta^2 E / \Delta v^2$) of solution of aluminum sulfate after addition of calcium gluconate.